

# METHYL ACRYLATE PRODUCTION

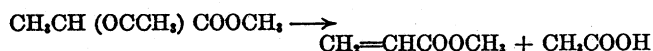
## By Pyrolysis of Methyl Acetoxypropionate 72

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Contact and construction materials used previously in the pyrolysis of esters are listed. A preliminary study is made of the influence of various metals, alloys, and other materials on the production of methyl acrylate by the pyrolysis of methyl acetoxypropionate. Quartz, Pyrex, Carborundum crystals, copper, carbon rods, crushed coke, and other relatively inert substances are satisfactory as packing for the pyrolysis tubes. Although the use of inert packing or contact materials appears beneficial on the basis of equal contact times, the beneficial effect is slight and even questionable when considered on the basis of equal addition rates. Nickel, Monel, alumina, silica, and iron actively catalyze the conversion of methyl acetoxypropionate into gas and carbonaceous material. Iron inactivated by intermittent treatment with steam is used satisfactorily in the pyrolysis. Small quantities of water in the methyl acetoxypropionate also inactivate the iron, but the formation of methyl acrylate is retarded simultaneously. Stainless steel (18% chromium-8% nickel) and 4-6% chromium steel appear suitable for the pyrolysis of methyl acetoxypropionate.

PREVIOUS articles (10, 11, 21, 48, 58) pointed out that methyl acrylate, an important resin (42) and synthetic rubber intermediate (5, 14, 34, 59, 63) can be made from several abundant carbohydrates by the following steps: (a) fermentative production (47) of lactic acid, (b) conversion (57) of lactic acid into methyl lactate, (c) acetylation of methyl lactate, and (d) pyrolysis (10, 56) of the acetylation product, methyl acetoxypropionate:



Considerable data regarding the effect of reaction temperature, time, and contact materials upon the pyrogenic conversion of methyl acetoxypropionate into methyl acrylate were reported in a recent paper (58). The present paper gives information obtained in a more extensive investigation of the effect of contact and construction materials upon the pyrolysis of methyl acetoxypropionate. The two principal aims of the investigation were to find contact materials with favorable catalytic action, and to determine which metals and alloys can be used satisfactorily in the construction of pyrolysis units. Data obtained with internal or dissolved potential catalysts will be presented in a later paper. Use of contact materials having selective catalytic effect would not only lower the pyrolysis temperature but would also have other advantages. It is particularly desirable to have information regarding suitability of construction materials because of the present cost and relative inaccessibility of certain metals and alloys.

Although the data in this paper were obtained with methyl  $\alpha$ -acetoxypropionate, it seems likely that some of the results may be applicable to the pyrolysis of other esters (32). The fact that products of great commercial value, such as acrylic esters and butadiene (16, 31) can be made by the thermal decomposition of appropriate esters adds to the importance of any information concerning ester pyrolysis.

### PREVIOUS INVESTIGATIONS

The effect of contact materials upon the thermal decomposition of methyl acetoxypropionate has been described only by Burns, Jones, and Ritchie (10) and by Smith and co-workers (58), who used Pyrex, quartz, alumina, silica gel, carbon rods, Carborundum crystals, porous clay chips, copper, and iron rods. Silica gel, alumina, and clay chips were found to catalyze the formation of gaseous by-products; the other materials appeared to be substantially inert and of approximately equal effectiveness. The results indicated also that a pyrolysis tube filled with inert packing was better than an empty tube. Since copper is claimed (7) to inhibit the polymerization of acrylic esters, the use of this metal might decrease the formation and subsequent carbonization of acrylic resins in the pyrolysis units.

Pertinent data regarding the use of contact materials have been obtained in the pyrolysis of compounds other than esters of lactic and acetoxypropionic acids. Chitwood (13) pyrolyzed esters of ethylene glycol, 1,2-propylene glycol, and 1,3-butylene glycol in glass or stainless steel tubes, packed in some instances with ceramically bonded alumina or ceramically bonded silica. He stated that inert packing materials, such as crushed sandstone, silica filter stone, and ceramically bonded fused aluminum oxide, can be used satisfactorily. Although the pyrolyses could be carried out at lower temperatures with catalysts such as activated alumina, vanadium oxide, molybdenum oxide, magnesium pyrophosphate, and zinc acetate, Chitwood reported that this procedure is not preferred because the catalysts are lacking in selectivity and catalyze side reactions.

According to Lichty (36) best results with respect to yield and purity were obtained when the catalyst was elementary copper, elementary nickel, copper sulfate, copper acetate, cuprous chloride, nickel sulfate, nickel acetate, nickel chloride, elementary copper in connection with iodine, and elementary nickel in connection with iodine in the ester to be pyrolyzed. He claimed also that quartz is effective as a catalyst when used in conjunction with iodine in the ester. Data reported by Lichty for the pyrolysis of cyanoisopropyl acetate are given in Table I.

Bilger and Hibbert (8) pyrolyzed several esters by passing their vapors through a quartz tube.  $\beta$ -Chloroethyl acetate was pyrolyzed in the presence of chloroacetic acid. The results indicated that the decomposition was not catalyzed by the chloroacetic acid.

Underwood and Baril (61) made an extensive investigation of the decomposition of esters mixed with anhydrous zinc chloride (0.5 mole zinc chloride per mole of ester). The resulting solution of zinc chloride was refluxed and then distilled. Ethyl formate, ethyl acetate, ethyl propionate, and ethyl *n*-butyrate were found stable when refluxed for 3 hours prior to distillation. When treated in the same manner, isoamyl *n*-butyrate yielded olefin and acid. Several other esters decomposed in a similar fashion. In every instance decomposition of the ester was effected in the presence of zinc chloride at a much lower temperature than when heated alone.

Adkins and Krause (2) studied the thermal decomposition of ethyl and isopropyl acetates over alumina, titania, and thoria at

TABLE I. PYROGENIC PREPARATION OF METHACRYLONITRILE (36)

Catalyst	Pyrolysis, %		
	350° C.	400° C.	Av. at 400° C.
Copper wire	26	72.7	73.3
		74.0	
Cu <sub>2</sub> Cl <sub>2</sub> , pumice	26	63.9	65.2
		66.5	
Quartz, ester contains 1% I <sub>2</sub>	29.8	66.8	66.8
		66.8	
Copper wire, ester contains 1% I <sub>2</sub>	32.4	76.5	75.4
		74.3	
Quartz	7.6	40.2	39.3
		38.4	

TABLE II. PYROLYSIS OF METHYL ACETOXYPROPIONATE OVER PYREX OR QUARTZ OR IN AN EMPTY PYREX TUBE

TABLE II. PYROLYSIS OF METHYL ACETOXYPROPIONATE OVER PYREX OR QUARTZ OR IN AN EMPTY TUBE											Yield, % of Theoretical				
Expt. No.	Av. Temp., ° C.	Pyrolysis Rate, Mole/Hr.		Free Space, Ml.	Contact Time, Sec.	Conversion to Methyl Acrylate, %			Conversion to Acetic Acid, %		Gases and Losses %	Acetic acid			
		Me acetoxypropionate	Me acetoxypropionate + N <sub>2</sub>			Observed	Corrected	From graph for corresponding: Time	Addition rate	Distn. analysis		Titration analysis	Me acrylate	Distn. analysis	Titration analysis
PYREX AND QUARTZ															
77	500	0.262	0.309	50	9.5	46.9	46.9 <sup>a</sup>	41.5	41.5	56.5	52.1	3.4	78.4	103.2	95.3
83	492	0.137	0.142	50	20.4	46.0	54.0 <sup>a</sup>	59	59	60.0	55.6	5.4	81.8	106.2	98.5
84	495	0.111	0.116	50	24.7	59.6	64.6 <sup>a</sup>	62.5	62.5	73.3	68.4	3.0	91.5	112.2	105.9
89	500	0.062	1.68	50	1.7	..	..	16	16	..	14.4	16.1	..	..	..
90	500	0.068	1.22	50	2.8	..	..	22	22	..	22.3	7.5	..	..	..
91	500	0.121	0.526	50	5.0	..	..	30	30	..	55.6	5.0	86.0	105.5	104.5
80	488	0.300	0.305	50	9.8	31.3	30.1 <sup>b</sup>	31	31	38.3	37.9	2.8	..	..	..
79	393	0.274	0.324	50	10.5	0	..	..	..	0	3.0	2.8	..	..	..
81	445	0.111	0.116	50	27.9	13.4	14.4 <sup>c</sup>	16	16	14.7	15.6	3.5	78.4	88.0	93.8
82	445	0.143	0.148	50	21.7	12.7	13.7 <sup>c</sup>	15	15	15.3	16.1	2.7	78.0	95.8	100.8
10 CC. QUARTZ															
50	570	0.577	0.582	82	7.3	76.1	..	..	..	86.9	86.9	8.2	85.0	96.9	96.9
5 CC. QUARTZ															
51	579	0.226	0.231	84	18.8	81.4	..	..	..	96.6	94.8	9.5	83.4	98.6	96.9
PYREX TUBING															
276	540	0.386	d	65	9.2	78.8	88.8 <sup>e</sup>	85	80	87.0	86.8	2.7	90.6	99.0	98.8
275	496	0.446	d	65	8.3	35.9	39.9 <sup>a</sup>	38.5	33	41.4	43.2	-1.0 <sup>f</sup>	91.5	105.6	110.4
274	499	0.396	d	65	9.4	28.7	29.7 <sup>a</sup>	41	35	31.2	33.0	9.8 <sup>g</sup>	71.0	77.2	81.6
EMPTY TUBE															
280	529	0.437	d	87	10.9	60.0	56.0 <sup>h</sup>	64	55	69.2	69.6	14.1	74.8	86.0	87.4
97	500	0.148	0.548	85	8.8	..	..	40	30	..	46.0	6.5	..	..	..
61 <sup>i</sup>	491	0.290	0.295	85	16.5	32.2	42.2 <sup>a</sup>	54	42	34.0	43.2	3.0	79.8	84.2	106.8
281	500	0.412	d	87	12.0	36.1	36.1	47	34	39.2	41.1	2.0	85.8	93.5	98.1
268	500	0.508	d	87	9.7	33.9	33.9	42	31	31.6	..	3.2	85.9	79.8	..
279	476	0.420	d	87	12.1	44.2	42.2 <sup>i</sup>	23	19	47.5	49.2	0.8	91.0	98.1	101.5
266	470	0.494	d	87	10.3	18.6	18.6	26	18	21.8	24.3	1.7	77.6	91.5	101.6
264	449	0.503	d	87	10.3	11.2	11.4 <sup>c</sup>	12	11	10.4	14.5	2.7	67.5	63.0	88.9
PYREX HELICES															
217	506	0.125	d	62	27.0	67.7	61.7 <sup>a</sup>	64	60.5	83.8	69.4	4.8	86.2	107.2	88.9
94	499	0.190	0.237	62	15.1	54.8	55.8 <sup>a</sup>	52.5	51.5	67.4	67.4	3.6	82.6	101.1	101.1
* Cor. to 500° C.    b Cor. to 485° C.    c Cor. to 450° C.    d No nitrogen used.    e Cor. to 550° C. f Small amount of reagent left in preheater from preceding run.    g Some reagent (about 10 ml.) left in preheater. h Cor. to 525° C.    i Citation (58), Table II.    j Cor. to 470° C.															

<sup>a</sup> Cor. to 500° C. <sup>b</sup> Cor. to 485° C. <sup>c</sup> Cor. to 450° C. <sup>d</sup> No nitrogen used. <sup>e</sup> Cor. to 550° C.  
<sup>f</sup> Small amount of reagent left in preheater from preceding run. <sup>g</sup> Some reagent (about 10 ml.) left in preheater.  
<sup>h</sup> Cor. to 525° C. <sup>i</sup> Citation (58), Table II. <sup>j</sup> Cor. to 470° C.

approximately 455° C. Olefins, acetic acid, acetone, and gases were obtained. It was concluded that the method of preparing the catalyst is as important as the particular element present in the catalyst, if not more so, and that saponification of the ester precedes decomposition.

Eyring (19) and co-workers discussed the theoretical aspects of Adkin's work (1, 2) on the decomposition of esters over alumina, thoria, and titania. Stevens and Richmond (60) proposed a mechanism for the decomposition of esters into a carboxylic acid and an unsaturated compound in the absence of catalyst.

Bachman and Tanner (9) claimed that copper used in connection with boric acid and copper borate are unusually efficient catalysts for the decomposition of esters into the corresponding acid and olefin. These catalysts were used, however, at 500°, 520°, and 550° C. in the reported experiments. According to van Pelt and Wibaut (45), acetates of primary alcohols decompose over glass wool in the absence of catalysts at 500° and 525° C.

Pyrolysis tubes made of the following materials have been used or suggested for the pyrolysis of esters: Copper (41), copper-lined (37), borosilicate glass (24, 26, 27), glass (13, 29, 30, 31), Pyrex (3, 25, 33, 38), iron (31, 43), platinum (46), quartz (8, 31, 49), silica (55), stainless steel (13, 24), and steel (31).

The following have been recommended or mentioned as catalysts or packing material: alkali acetate (18), alumina (1, 2, 35, 39, 40, 53, 54), activated alumina (13), ceramically bonded alumina (13), aluminum chloride (liquid-phase experiments) (22, 23), aluminum phosphate (35), bauxite (35), boric acid on metallic copper (9), boric acid supported by silica gel (37), boric anhydride (53), boron oxide supported by silica gel (37), active carbon (31), carbon particles (4), ceramic substances (4), charcoal (4), clay (35), coke (35), copper (36, 38), copper acetate (36), copper in connection with iodine (36), copper sulfate (36), cuprous chloride (36), unglazed earthenware beads (25, 26), unglazed earthenware rings (24, 31), glass rings (3, 12, 29, 30), glass wool (15, 17, 45), graphite (35, 50, 51, 52), iodine (6), scrap iron (4), kaolin (16), magnesium pyrophosphate (13), molybdenum oxide (13), nickel (36, 44), nickel acetate (36), nickel chloride (36), nickel in connection with iodine (36), nickel sulfate (36), phosphoric acid (18, 37), pumice (54), pumice containing sulfuric acid (54), quartz (31, 35), quartz chips (4, 31, 50, 51, 52), ceramically bonded silica (13), silica gel (10, 31, 50, 51, 52), sodium metaphosphate (37), stainless-steel Lessing rings (24, 26, 27), steel shav-

ings (31), sulfuric acid (18, 28), thoria (2, 39, 40, 55) porous tile (62), titania (2, 39, 40, 53), vanadium oxide (13), zinc acetate (13), zinc chloride (18, 61), and zinc oxide (39, 40).

Some information has been published regarding the behavior of acetic acid, which is formed in the decomposition of methyl acetoxypropionate and other esters, in the presence of contact materials at high temperatures (53). When pyrolyzed over finely divided copper at 390° to 410° C., acetic acid yielded gas comprising seven volumes of carbon dioxide to one of methane. Some acetone was formed (53). An analogous decomposition occurred rapidly with reduced nickel at temperatures above 320° C. In another investigation (53) vapors of acetic acid were passed over barium carbonate heated to about 500° C. The products were acetone, water, and carbon dioxide. Zinc oxide or carbonate and the carbonates of calcium and strontium had a similar effect.

#### EXPERIMENTAL PROCEDURE

The data of Tables II and III were obtained with the pyrolysis equipment described in an earlier paper (58). The Pyrex pyrolysis tube (2.5 cm. outside diameter) was heated electrically over a 30-cm. length. Approximately 85 ml. of packing were required to fill the heated portion of the tube. Temperature was measured as before with two thermocouples located in a central well and outside the tube wall. The reported values are the average of the temperatures indicated by the two thermocouples. The contact time was based on the total free space in the tube and the assumption that no change in volume occurred. The pyrolysis products were analyzed as before (58) by distillation and by titration for acid content. The yield of acetic acid was calculated from the titration data on the assumption that acetic acid was the only acid present. The yields of methyl acrylate and acetic acid were calculated from the distillation curve on the assumption that all the material distilling below 100° C. was methyl acrylate and all distilling between 100° and 140° was acetic acid. In most instances the distillation curves were characterized by distinct plateaus that could be used to estimate the proportions of

methyl acrylate, acetic acid, and unchanged methyl acetoxypropionate in the liquid product. When the contact material promoted side reactions, however, the plateaus were less distinct or absent because of the presence of by-products. When appreciable amounts of low-boiling by-products were formed, the yields reported are high since all the material distilling up to 100° was taken as methyl acrylate. The yields (as per cent of theoretical) shown in the tables were calculated on the basis of the methyl acetoxypropionate destroyed in the pyrolysis. Since experimental errors were multiplied in these calculations, these yield data are less accurate than the data which represent the proportion of the reagent converted per pass into methyl acrylate.

To obtain information regarding the adequacy of the distillation data in calculating yields of methyl acrylate, saponification numbers were determined for the 25° to 100° fraction of two pyrolysis products. The titration and saponification data indicated that the sample characterized by a distinct distillation plateau had a methyl acrylate content of 99%. According to the saponification data, the second sample, believed to be less pure because of its distillation behavior, contained 95% methyl acrylate. By direct titration it was shown that both of the 25° to 100° fractions contained less than 1% acetic acid.

Although the free volume of the pyrolysis zone ranged from 40 to 85 ml., the amount of methyl acetoxypropionate pyrolyzed in most of the experiments was only 25 to 60 grams. It is believed that the use of larger quantities of methyl acetoxypropionate would have given better yields and more reproducible results.

To eliminate effects that might be due to size and shape of the packing, several metals and alloys (experiments 208, 210, 212, 213A, 214, 215, 216, 218, 219, and 220, Table III) were used in the form of gauze or screening (7-mm. squares of 20-mesh screening prepared from B and S No. 26 gage, 0.016-inch diameter, wire).

Pyrex was studied as an empty pyrolysis tube and as short lengths of tubing, and rings or helices (2-mm. diameter) were used as packing (20). Both aluminum shot and aluminum gauze were studied. Coke was made by carbonizing thick Freeport coal at 900° C. The liquid product obtained in the first experiment using coke (experiment 86) was light brown and probably contained by-products. The coke appeared to behave satisfactorily, however, in experiment 87. A catalyst similar to that described by Bachman and Tanner (9) was made by packing the pyrolysis tube with copper screening and dusting the screening thoroughly with boric acid. The first run with this catalyst yielded some water, but after the first run the catalyst appeared conditioned and satisfactory. During the pyrolyses, the active packing materials caused the formation of large amounts of gas and carbonaceous matter. Even the "inert" contact materials became coated with a thin layer of carbon or carbonaceous matter. Additional information regarding the characteristics of the packing materials is given in Tables II and III.

During some of the pyrolyses, nitrogen was passed through the pyrolysis tube along with methyl acetoxypropionate. The rate of adding the nitrogen was 0.005 mole per hour in most of these experiments, but 0.047 mole per hour in a few.

#### PACKED TUBE EXPERIMENTS

To compare the data in Tables II and III with those reported in an earlier paper (58) and obtained with quartz and Pyrex packing, the earlier data were replotted to give the conversion to methyl acrylate as a function of contact time based on the free space and also as a function of the rate of reagent feed. The latter relation is shown in Figure 1.

The conversion data obtained with various contact materials (Tables II and III) were corrected to 450°, 470°, 485°, 500°, 525°, or 550° C. with the aid of data from the earlier paper (58, Figure 3). The corrected data were then compared with the conversion data previously obtained (58) on the basis of equal contact times (based on free space) and also on the basis of equal

reagent addition rates. Probably the relation of conversion per pass to the rate of addition of reagent is more important from a commercial or engineering standpoint than the influence of contact time on conversion.

When the results in Table II are compared on the basis of equal contact times, it is seen that the tubes packed with inert contact materials are more effective than an empty Pyrex tube in promoting the conversion of methyl acetoxypropionate to methyl acrylate. The efficacy of the inert packing appears less impressive, however, when the results are compared on the basis of equal addition rates. For example, the conversion in an empty Pyrex tube (experiment 61) after correction to 500° C. was 42.2%, whereas at the same addition rate about 42% conversion would be expected with the tube packed with quartz and Pyrex. With one exception (experiment 279), when compared on the basis of equal contact time, each empty-tube experiment showed a lower conversion than a packed tube. On the basis of equal addition rates, however, the difference disappeared. In run 279 the temperature readings were somewhat uncertain, and the average temperature might have been higher than that reported.

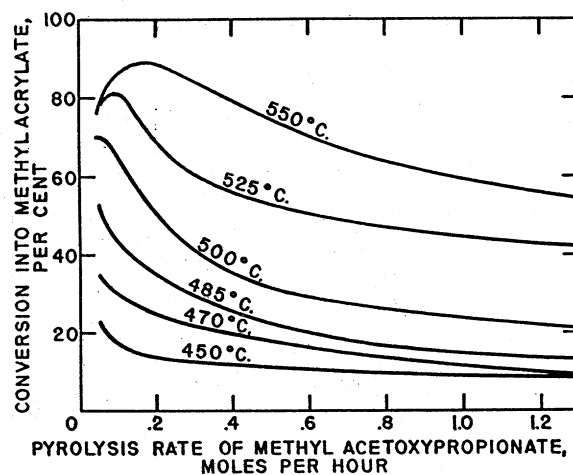


Figure 1. Conversion of Methyl Acetoxypropionate to Methyl Acrylate as a Function of Pyrolysis Rate

Whether the slight beneficial effect of the inert packing should be attributed to wall effects or to improved heat transfer that resulted from turbulence in the vapor stream is not known.

Aluminum screen, Monel (nickel-copper alloy) screen, nickel screen, alumina, silica gel, and clay chips caused the formation of considerable gas (Table III); hence these materials cannot be considered inert and suitable as packing. Nickel, alumina, and silica gel promoted the formation of gases even below 400° C. Although the data in Table III do not demonstrate that ordinary iron and steel are catalytic, it was observed in later experiments that iron actively catalyzes the production of gases and carbonaceous material. It should be noted (experiments 68, 210, and 211, Table III) that aluminum was much more catalytic at 550° C. than at 500°. Pearce (44) reported that nickel promotes the conversion of simple esters into gases. It is of interest that the nickel in stainless steel (18% chromium-8% nickel) was inactive, whereas the nickel-containing alloy, Monel, was highly catalytic.

The observation that nickel promotes the formation of gaseous and carbonaceous by-products seems at variance with the claim of Lichty (36) that nickel has a beneficial effect in the decomposition of esters into carboxylic acid and olefin.

Although little effort was expended in identifying the by-products when nickel, alumina, Monel, pumice, and silica gel were used as packing, acetaldehyde and water were obtained in some of these experiments. Considerable quantities of carbonaceous matter were formed on the active contact materials, such as

TABLE III. PYROLYSIS OF METHYL ACETOXYPROPIONATE OVER VARIOUS CONTACT MATERIALS

TABLE IX. PROPERTIES OF METHYL ACRYLATE OBTAINED OVER VARIOUS CONTACT PERIODS																
Expt. No.	Av. Temp., ° C.	Pyrolysis Rate, Mole/Hr.		Contact Material	Free Space, ML	Con- tact Time, Sec.	Conversion to Methyl Acrylate, %			Converted to Acetic Acid, %		Gases and Losses, %	Yield, % of Theoretical Acetic acid			
		Me acetoxy- propio- nate	Me acetoxy- propio- nate + N <sub>2</sub>				Ob- served	Cor- rected	From graph for corresponding: Time	Addition rate	Acetic analysis		Titra- tion analysis	Me acrylate	Distn. analysis	Titra- tion analysis
58 <sup>a</sup>	502	0.282	0.287	Carbon rods	40	7.9	42.3	40.3 <sup>b</sup>	38	42.5	54.3	53.7	2.9	83.4	106.9	105.8
59	543	0.292	0.297		40	7.2	79.5	86.5 <sup>c</sup>	81.5	84.5	88.2	88.8	6.6	92.5	99.3	100.0
86	497	0.244	0.249	Coke, lumps	65	15.2	58.1	61.1 <sup>b</sup>	52.5	46	51.7	43.4	5.5	96.1	86.4	72.6
87	497	0.240	0.245		65	15.1	50.9	53.9 <sup>b</sup>	52.5	46.5	54.2	52.4	6.5	87.0	92.9	89.8
65 <sup>a</sup>	494	0.287	0.292	Carborundum	37	7.3	37.7	43.7 <sup>b</sup>	36	42	45.3	44.5	3.1	81.6	98.8	97.0
39 <sup>a</sup>	550	0.112	0.117	crystals	68	31.0	84.3	84.3	85	87	103.1	..	6.3	84.3	103.1	..
66 <sup>a</sup>	493	0.235	0.240	Clay chips	47	11.2	17.4	24.4 <sup>b</sup>	45	46	30.3	36.2	15.6	23.2	40.0	47.9
92	499	0.109	0.168	Pumice	60	21.9	65.4 <sup>d</sup>	66.4 <sup>b</sup>	60	57	73.0	..	7.2	68.0	75.8	..
95	350	0.120	0.167	Alumina pellets	40	16.9	..	..	..	..	..	..	30.0	..	..	..
96	348	0.183	0.220	Silica gel	50	15.3	..	..	..	..	..	..	28.4	..	..	..
64 <sup>a</sup>	494	0.246	0.251	Copper screen	74	16.9	47.4	53.4 <sup>b</sup>	54.5	46	52.2	54.9	3.3	88.6	97.5	102.5
213	500	0.110	0.115		71	35.0	61.6	61.6 <sup>b</sup>	67.5	63	67.6	66.3	2.9	91.0	99.2	97.4
213A	498	0.118	0.123		71	32.8	55.2	57.2 <sup>b</sup>	67	62	65.0	65.0	4.6	81.0	95.2	95.2
67 <sup>a</sup>	496	0.247	0.252		74	16.7	35.4	39.4 <sup>b</sup>	55	45	58.8	55.9	2.8	65.2	108.0	102.6
C1	482	0.558	..	Copper and boric acid	74 <sup>i</sup>	7.5	45.4	41.8 <sup>i</sup>	20	17	46.9	51.2	2.2	83.0	86.6	94.8
C2	497	0.548	..		74 <sup>i</sup>	9.7	43.6	46.6 <sup>b</sup>	44	30	45.7	47.5	0	92.8	96.7	100.5
73 <sup>a</sup>	496	0.273	0.278	Steel rods	40	8.2	38.0	42.0 <sup>b</sup>	38.5	43	36.7	35.4	6.0	87.2	84.6	81.6
85	496	0.253	0.258	Iron tacks	58	12.8	42.2	46.2 <sup>b</sup>	48.5	45	45.4	36.3	5.7	87.6	93.3	74.5
220	504	0.151	0.156	Steel screen	70	25.4	54.7	50.7 <sup>b</sup>	63	57	54.6	..	7.8	80.4	80.0	..
208	500	0.107	0.114	Stainless steel	72	35.9	43.0	43.0 <sup>b</sup>	67.5	63.5	75.7	68.4	4.0	70.2	124.4	112
209	550	0.133	0.138	screen	72	27.8	82.5	82.5 <sup>b</sup>	86	88	108.6	94.5	6.2	82.5	108.6	95.4
98	485	0.189	0.236	Stainless steel	65	15.9	70.2	70.2 <sup>b</sup>	36	34	58.7	60.2	8.2	95.2	79.7	81.3
99	485	0.215	0.262	helices	65	14.4	..	..	35	33	..	65.4	5.8	..	..	..
100	487	0.184	0.231		65	16.3	66.0	64.0 <sup>b</sup>	36.5	33.5	67.4	66.2	8.0	85.6	91.8	90.0
214	498	0.129	0.134	Brass screen	68	28.8	50.6	52.6 <sup>b</sup>	65	60	57.8	54.4	5.2	84.0	95.8	90.3
215	498	0.099	0.104	Everdur screen	70	38.2	59.4	61.4 <sup>b</sup>	68	65	65.1	61.4	4.0	88.0	95.8	90.8
68 <sup>a</sup>	502	0.260	0.265	Al shot	40	8.4	38.1	36.1 <sup>b</sup>	39.5	44.5	45.7	46.4	3.6	82.1	95.3	96.8
210	500	0.126	0.131	Aluminum	70	30.3	76.3 <sup>d</sup>	76.3	66	60	56.7	52.6	10.2	117.6	86.8	80.6
211	550	0.124	0.129	screen	70	28.9	..	..	86	88	40.4	43.3	20.8	..	40.4	43.3
216	502	0.114	0.119	Monel screen	70	33.4	..	..	67	61.5	..	..	86.3	..	..	..
218	502	0.147	0.152	Nickel screen	71	26.5	..	..	63.5	57	..	..	100	..	..	..
219	397	0.130	0.136		71	29.8	..	..	..	..	..	..	27.0	..	..	..

<sup>a</sup> Citation (54), Table I. <sup>b</sup> Cor. to 500° C. <sup>c</sup> Cor. to 550°. <sup>d</sup> No good plateau for methyl acrylate; evidence for water-acrylate azeotrope.

<sup>e</sup> No plateaus at 80° C. but all distillate collected below 90° was considered methyl acrylate; considerable acetaldehyde formed.

<sup>f</sup> Plateau at 55° C.; this cut tentatively identified as methyl acetate; acetaldehyde also identified.

<sup>g</sup> Considerable acetaldehyde formed. <sup>h</sup> No nitrogen used.

<sup>i</sup> When the packing was removed after run C2, the copper screen was coated with a glossy solid, hence the free space may be lower than that recorded.

<sup>j</sup> Cor. to 470° C. <sup>k</sup> Cor. to 485° C. <sup>l</sup> No plateau at 80° C.; plateau at 70° (water-acrylate azeotrope).

nickel and alumina. The composition of some of the gaseous by-products is given in Table IV.

With the exception of the data obtained in experiments 98, 99, and 100, the results (Table III) indicate that all the inert materials studied (quartz, Pyrex, etc.) were about equally effective as contact materials.

Although some of the contact materials (nickel, alumina, etc.) promoted the decomposition of methyl acetoxypropionate into gases, no material was found that appeared appreciably to catalyze decomposition into the desired products, methyl acrylate and acetic acid.

Although most of the data in Table III suggest that the value of packing in the pyrolysis of esters is questionable, it should be pointed out that only a few conditions were studied and that some contact materials might be found decidedly advantageous under other conditions.

Experiments 98, 99, and 100 (Table III) indicate that small stainless steel helices (20) which have high free space and surface, were definitely beneficial at 485° C. The Pyrex glass helices at 500° displayed no such effect (experiment 94, Table II), but the glass helices were larger and had less surface than the stainless steel helices. These results are interesting; but from the standpoint of maximum production of methyl acrylate per unit time and on the basis of data thus far obtained, it does not seem pref-

erable to operate at 485° with helices rather than at 525–550° C. with an empty tube or some other inert packing.

The catalytic behavior claimed for a copper-boric acid catalyst by Bachman and Tanner (9) was not observed when this packing was used in the decomposition of methyl acetoxypropionate (experiments C1 and C2, Table III).

The discussion thus far has been concerned primarily with the effect of contact material upon the conversion per pass of methyl acetoxypropionate to methyl acrylate. Although some discrepancies are apparent, the relatively inert packing materials were characterized in most instances by relatively high yields. In this connection, yields of methyl acrylate of 90% and higher have been obtained in this laboratory with a stainless steel pyrolysis unit and larger quantities of methyl acetoxypropionate.

#### EFFECT OF CONSTRUCTION MATERIALS

Several experiments were carried out to determine whether ordinary iron, 18–8 stainless steel, and 4–6% chromium steel are suitable for equipment to be used in the commercial pyrolysis of methyl acetoxypropionate. Iron was studied because of its relative availability and low cost; 4–6% chromium steel was studied primarily because this alloy has been widely used in the construction of petroleum cracking units. Relatively little chromium is needed for the production of 4–6% chromium steel, and it has been considered possible that a discarded or idle cracking unit made of this or a similar alloy might be used, as such or after minor modifications, to pyrolyze methyl acetoxypropionate on a commercial scale.

The behavior of the three metals in the pyrolysis tube was compared in one series of experiments using a modification of the apparatus previously employed. In the heated zone (2.5 cm. in diameter and 30 cm. long) of the Pyrex tube was suspended a 30-cm. length of pipe of the metal being tested; many 3-mm. holes were drilled into the pipe to afford more surface and aid free circulation of the gaseous reactant and products. The main pur-

TABLE IV. COMPOSITION OF GAS FORMED IN THERMAL DECOMPOSITION OF METHYL ACETOXYPROPIONATE OVER ACTIVE CONTACT MATERIALS

Expt. No.	Gaseous Catalyst	Gas, Moles/Mole Me Acetoxypropionate Pyrolyzed					
		Total	CO <sub>2</sub>	CO	Unsatd. hydrocarbons	H <sub>2</sub>	Satd. hydrocarbons
211	Al	0.49	0.25	0.14	0.06	..	..
216	Monel	4.5	0.53	1.54	6.07	2.18	0.11
218	Ni	3.4	0.56	1.14	..	1.56	..
219	Ni	1.15	0.23	0.45	..	0.39	..

<sup>a</sup> Less than 0.05 mole.

TABLE V. EFFECT OF CONSTRUCTION MATERIALS ON PYROLYSIS OF METHYL ACETOXYPROPIONATE

Expt. No.	Av. Temp., ° C.	Contact Time, Sec.	Liquid Products, % of Starting Material	% Conversion to:			Yield, % of Theoretical			% Me Acetoxy- propionate Recovered
				Me acrylate	Acetic acid		Me acrylate	Acetic acid		
					Distn. analysis	Titration analysis		Distn. analysis	Titration analysis	
IRON PIPE										
225	500	18.1	99.0	45.5	68.0	45.6	63.5	95.3	66.2	28.6
226	499	16.6	98.3	29.5	47.4	43.4	67.3	107.8	98.6	55.6
227	525	19.9	94.6	55.4	69.1	72.0	77.1	96.9	100.8	28.4
228	525	18.6	94.8	49.9	71.6	75.7	65.2	93.2	96.7	23.5
229	550	21.3	86.2	61.5	64.3	66.8	74.2	77.8	80.7	17.2
230	550	20.1	62.8	29.6	36.6	39.0	34.5	42.7	45.5	14.1
231	550	13.2	55.0	19.6	26.2	28.5	25.8	34.7	37.8	24.3
232*	550	14.6	75.2	27.5	44.1	45.9	34.7	55.6	57.8	20.7
233	550	16.4	78.2	49.9	63.4	59.0	58.8	75.0	69.7	15.1
234	550	13.5	76.4	48.4	49.9	48.4	64.0	65.8	63.8	24.4
235	550	14.5	79.5	54.2	56.9	57.8	66.9	70.3	71.4	19.1
236	500	17.7	93.0	33.1	45.3	43.6	71.0	97.0	93.2	53.4
237	550	15.5	87.9	55.2	77.3	72.5	62.8	87.7	82.4	11.9
STAINLESS STEEL PIPE										
238	550	40.5	91.9	68.1	102.5	91.1	70.1	105.4	97.8	2.8
239	550	28.2	96.3	49.6	70.4	68.1	71.2	101.0	99.0	30.5
240	550	24.5	92.2	65.0	82.4	78.1	74.6	94.5	89.5	12.7
241	526	29.7	94.6	58.1	63.0	70.0	84.8	92.0	102.0	31.7
4-6% CHROMIUM STEEL PIPE										
247	499	26.3	97.9	32.1	60.9	58.8	61.0	115.6	111.6	47.3
248	547	27.3	95.4	55.8	91.8	90.0	65.2	108.4	106.3	15.4
249	590	32.0	82.3	40.7	92.8	86.4	42.1	96.4	99.5	3.4
250	576	28.8	93.5	58.1	97.2	97.2	62.8	105.0	105.0	7.4
251	550	34.3	93.6	54.0	103.9	97.4	57.9	111.6	104.9	7.0

\* Before this run, carbon deposit was removed from the iron pipe.

pose was to find whether these metals promote the formation of by-products, and no real attempt was made to determine whether iron and the alloys were seriously corroded by the acetic acid formed in the decomposition.

Analyses were made as before by distillation and titration of the pyrolysis products. Temperature was measured by a chromel-alumel thermocouple located between the furnace and the glass tube.

Table V shows that the recovery of liquid products, which is a measure of the tendency of the metal to promote gas formation, is lowest for the iron, indicating the greatest catalytic activity for this material. The iron pipe was weighed before and after each experiment, and it was found that in the runs marked by catalytic activity several grams of a black carbonaceous matter was deposited on the pipe. Apparently the deposit was an agent in the catalytic activity, since removal of the deposit increased the recovery of liquid products (experiment 232). After run 237 the pipe was scraped clean, and its weight was unchanged within 0.1%.

Both the stainless steel and the 4-6% chromium steel pipes gave satisfactory recovery of liquid products, although the latter showed some catalytic activity at 590° C. The stainless steel gave the highest yields of methyl acrylate.

In order to investigate further the undesirable catalytic effect of iron, an iron pyrolysis chamber was built and operated. Except for the use of iron, this apparatus was similar to that used

previously (58). Temperatures were measured by one thermocouple in a well extending into the heated zone and by another between the pyrolysis tube and furnace. During a run the temperature gradient usually was about 30°, the higher temperature being at the outer couple. From the results obtained with the iron pyrolysis unit (Table VI), it is apparent that initially the iron tube had no appreciable adverse catalytic effect. When the tube was operated at 575° C., however, liquid recovery fell off, and the yields of both methyl acrylate and acetic acid were lowered. This behavior persisted at lower temperatures, suggesting that once iron is "activated", it retains its activity even at lower temperatures. However, flushing the tube with steam

and air removed the activity as shown by experiments IP10 and IP11. Figure 2, in which the permanent gas collected in experiment IP12 is plotted as a function of time, shows that the tube became reactivated on further use. At the close of experiment IP12 the tube was markedly catalytic, but flushing with steam alone reduced the activity, as shown by experiment IP13.

The fact that intermittent treatment with water alone inhibited the catalytic activity of the iron suggested the use of a solution of water in methyl acetoxypropionate. Accordingly, methyl acetoxypropionate containing 2% by weight of distilled water was pyrolyzed in the iron apparatus under conditions similar to those used with pure methyl acetoxypropionate. The results (Table

TABLE VI. PYROLYSIS OF METHYL ACETOXYPROPIONATE IN IRON EQUIPMENT

Expt. No.	Temp., ° C.	Contact Time, Sec.	Liquid Products, % of Starting Material	% Conversion to:			Yield, % of Theoretical			% Me Acetoxypropionate Recovered
				Me acrylate	Acetic acid Distn. analysis	Acetic acid Titration analysis	Me acrylate	Acetic acid Distn. analysis	Acetic acid Titration analysis	
IP1	500	16.7	94.2	28.4	44.0	47.3	61.5	95.2	109.3	53.9
IP2	500	13.3	97.0	23.8	42.7	47.6	61.2	110.0	110.4	61.1
IP3	525	15.6	96.8	44.6	63.6	68.6	68.3	98.0	113.6	37.8
IP4	525	16.3	96.1	43.6	61.3	62.8	75.9	106.4	108.9	42.4
IP5	550	14.8	93.6	60.2	75.9	85.8	74.8	103.0	105.5	26.5
IP6	550	14.8	93.0	55.0	79.6	72.6	73.6	106.5	96.4	25.1
IP7	575	10.9	77.1	48.3	61.0	67.8	57.8	73.0	81.2	16.5
IP8	545	15.4	48.0	18.6	15.2	16.9	26.0	21.3	23.7	28.6
IP9	520	15.1	54.4	6.7	9.6	37.3	12.0	17.1	66.6	43.8
IP10 <sup>a</sup>	550	15.2	91.9	59.6	70.2	77.6	76.1	89.8	97.7	21.7
IP11 <sup>b</sup>	550	10.5	93.4	60.0	70.8	83.0	79.3	93.4	109.0	24.8
IP12	550	18.8	93.0	58.1	74.0	78.4	77.9	99.3	107.5	25.8
IP13 <sup>c</sup>	550	14.2	92.1	58.4	72.6	75.0	77.0	95.6	98.9	24.2

<sup>a</sup> Before this run water was pumped through at reaction temperature, followed by a blast of air.

<sup>b</sup> Before this run 25 ml. of water were pumped through at reaction temperature, followed by air for 1 hour at the rate of 25,000 ml. an hour.

<sup>c</sup> Before this run 30 ml. of water were pumped through at reaction temperature; contact time was 2 seconds.

TABLE VII. PYROLYSIS OF METHYL ACETOXYPROPIONATE-WATER MIXTURES IN IRON EQUIPMENT

Expt. No.	Temp., ° C.	Contact Time, Sec.	Liquid Products, % of Starting Material	% Conversion to:			Yields, % of Theoretical			% Me Acetoxypropionate Recovered	
				Me acrylate	Acetic acid Distn. analysis	Acetic acid Titration analysis	Me acrylate	Acetic acid Distn. analysis	Acetic acid Titration analysis	In presence of water	In absence of water <sup>a</sup>
IP14	520	13.8	92.9	27.4	32.0	34.5	68.7	80.2	86.6	60.0	43.8
IP15	520	9.5	96.6	22.6	28.1	30.2	72.4	90.0	96.9	68.7	43.8
IP16	555	11.8	95.3	30.5	36.6	37.2	75.5	90.4	91.9	59.7	..
IP17	550	13.2	96.3	33.9	40.1	41.4	76.7	91.0	94.2	55.9	24.2
IP19	565	11.9	96.5	33.4	39.2	41.2	81.6	97.3	98.0	58.4	24.3
IP20	600	12.5	62.6	20.1	22.8	23.9	34.1	38.8	40.7	41.2	..

<sup>a</sup> Under similar conditions of temperature and contact time.

VII) indicate that water inhibits materially the catalytic effect of the iron, but also inhibits the conversion into methyl acrylate and acetic acid. Even at 565° C. the recovery of liquid products was high and gas formation was not excessive, although at 600° the recovery of liquid products fell off. The onset of gas evolution was fairly sudden at 600°, as shown in Figure 2. For the first 40 minutes the rate of gas evolution was more or less normal, after which the rate increased approximately fourteen fold.

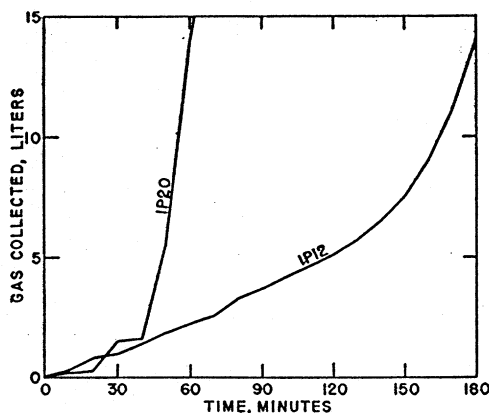


Figure 2. Formation of Permanent Gas as a Function of Time

IP12, pure reagent, 550° C.  
IP20, reagent-water mixture, 600° C.

The products obtained by pyrolyzing a mixture of methyl acetoxypropionate and water differed in distillation behavior from the products of the water-free pyrolyses. The water and methyl acrylate distilled azeotropically at about 70° C., most of the distillate consisting of methyl acrylate. The distillate separated into a large upper layer and a small lower layer, which were composed mainly of methyl acrylate and water, respectively.

It may be concluded that stainless steel of the 18-8 type and 4-6% chromium steel can be used to construct equipment suitable for the pyrolysis of methyl acetoxypropionate and that ordinary iron can be used if its tendency to promote the formation of gaseous by-products is controlled by treatment with steam. Whether intermittent treatment with steam is preferable to the continuous use of water-methyl acetoxypropionate solutions is not known. Presumably iron-chromium alloys containing more than 4-6% chromium also would be satisfactory. Possibly iron and alloy equipment would become conditioned in service and have more suitable properties after being used for a considerable time. Amines, sulfur compounds, or other chemicals might be found preferable to water in retarding the formation of gas.

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